

THE DIPOLE MOMENTS AND STRUCTURES
OF ORGANIC PEROXIDES AND RELATED SUBSTANCES

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I. Introduction

This dissertation describes the results of a study of the structures of an important group of organic compounds containing the peroxy grouping, $-O-O-$. The method of study used here has been the estimation of the dipole moments of these compounds from measurements of the dielectric polarization and molecular refractivity of their dilute solutions in a non-polar solvent.

The special advantages of this type of study have been set forth in several well known monographs such as those by Debye (1), Smyth (2), and Le Fevre (3). Among the advantages of the method for the compounds studied in this research should be mentioned the fact that it provides a means of detecting the presence of groupings of high polarity and should be helpful in distinguishing between branched and unbranched structures, such as $\overset{O}{\underset{\cdot}{\underset{|}{O}}}-$ and $-O-O-$ that have been proposed for the peroxy group. It is also one of the best methods of study of intramolecular rotation which is an important problem in the structure determination of the peroxides because of the non-linearity of the arrangement of the linkages attached to the peroxy part of these molecules. Furthermore, it often yields information concerning intermolecular association from the manner of the dependence of the polarization upon the concentration. These advantages of the method were shown

in a study of polysulfides carried out recently in this Laboratory (4) and because of the close relationship of some of the structural features of the polysulfides and the peroxides, this method appeared attractive for study of the latter also.

Indeed, as will be shown below, the determination of the dipole moment of the parent substance, hydrogen peroxide, by Linton and Maas (5) has aided greatly in elucidation of its structure. Furthermore, no systematic study of the organic peroxides had been made by the dipole moment method at the time this research was contemplated, the only published measurements being those of Oesper and Smyth (6) on dibenzoyl peroxide, although there appeared shortly after the start of the present work a study of a small group of peroxides including di-t-butyl peroxide, t-butyl hydroperoxide and ascaridole, by Rogers and Campbell (7).

The compounds whose investigation is reported in this dissertation are the following: di-t-butyl peroxide, t-butyl hydroperoxide, cumene hydroperoxide, dibenzoyl peroxide and perlauric acid. These include representatives of the four most important classes of organic peroxides, viz., hydroperoxides, dialkyl peroxides, diacyl peroxides and peracids, and this study is to the best of our knowledge the first systematic structure study of these groups. It is planned to continue this study in this Laboratory to

cover more examples of these types and closely related peroxy compounds.

Hydrogen Peroxide

Hydrogen peroxide may be regarded as the parent substance for the peroxy compounds. For this reason it is advantageous to discuss its structure first.

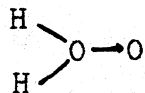
The chemical properties of hydrogen peroxide: its various reactions, oxidative, reductive, and synthetic, and its decomposition by catalytic and photochemical means present such a large and conflicting body of information that it is impossible to use this information as the sole basis of a structure assignment.

Physical investigation has proven more useful in eliminating many of the structures proposed for hydrogen peroxide and in providing more geometric detail for the acceptable configurations. A good historical summary of the structures that have been suggested for hydrogen peroxide can be found in the book by Machu (8).

At the present time the most widely accepted model for the arrangement of the atoms in hydrogen peroxide is that proposed by Penney and Sutherland (9). It is a skew structure with a C_2 point grouping. Their calculations show that the azimuthal angle between the planes of the two -OH groups bonded together by the O-O axis is determined primarily by the interaction of the electronic

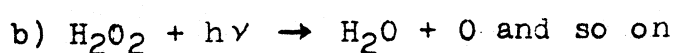
distributions about the two oxygen atoms. In forming the strongest possible bonds between the oxygen atoms, the charge density on these atoms becomes unsymmetric about the O-O axis and, together with all the other types of interaction, fixes the azimuthal angle at about 100° as the most stable position. Similarly, the H-O-O bond angle turns out to be 100° for their structure. This interaction is also calculated by them to be the most important one in preventing free rotation of the hydrogens about the O-O axis, with the result that a rather fixed skew structure exists, the azimuthal angle and the bond angle both being 100° . These angles are shown in Figure 1, structure I.

Practically all of the infrared and Raman spectral data have been correlated with this model (10,11) and the dipole moment value measured by Linton and Maas (5) supports this structure. However, as Herzberg (12) has pointed out, according to Hellmann (13) the model



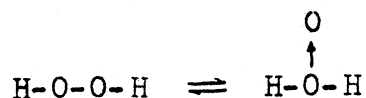
is also possible, on the basis of these data. Theilacker (14) has shown that the dipole moment can also be explained with a free-rotation model. This model would, however, result in additional unbound frequencies in the Raman and infrared spectra (10).

The equality of the two oxygen atoms remains in debate in the literature on hydrogen peroxide despite the evidence in favor of this equality. It is interesting that study of the photochemical decomposition of this substance (15) suggests two mechanisms which support both the branched and unbranched structures:



Tautomerism has been suggested by Quartaroli (8)

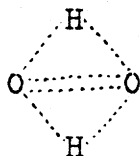
for instance,



and Geib and Harteck (16) believed that they obtained a new form of hydrogen peroxide through the action of hydrogen atoms on oxygen at low temperature. This form, according to them, changes over to the normal form at -115°C , with partial decomposition.

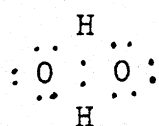
The ultraviolet absorption measurements by Riecke (17) do not support the assumption of the existence of tautomeric forms, and Neiding and Kazarnovskii (18) obtained magnetic data which do not bear out the alleged existence (16) of a different modification of H_2O_2 below -110°C .

The model of Rius (19) should be mentioned here because it has a formal similarity to a model to be proposed in this dissertation:

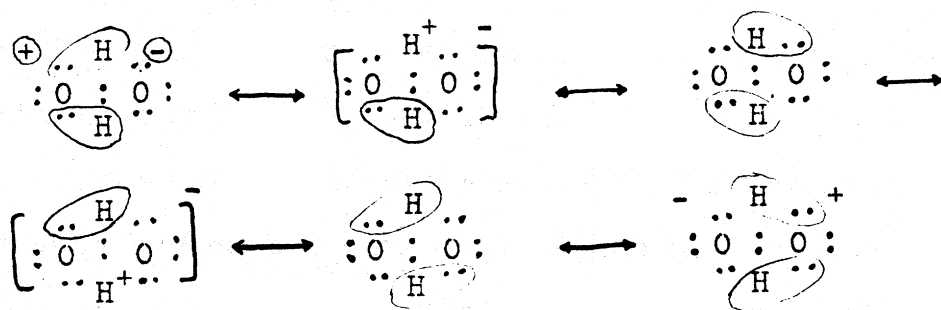


The model proposed in this dissertation is a folded structure with a C_{2v} point group in which each of the hydrogen atoms is equidistant from the two oxygen atoms and in which the dihedral angle between the planes of the hydrogen atoms might be equal to that for the Fenney and Sutherland model. This model is pictured in Figure 2.

The electronic structure may be written



based on the following resonant forms:



As a result of this resonance the O-O bond would have partial double bond character, which is in agreement with the high molecular refraction observed for hydrogen peroxide and for which the Fenney and Sutherland structure does not offer explanation. The refraction equivalent of a double bond (20) for the D-line is 1.733 cc. The exaltation observed for hydrogen peroxide is equal to $2.19 - 1.529 = 0.661$ cc., indicating a large amount of double bond character.

The resonance would also account for the weakening of the O-O bond in alkaline media (21). Assuming that the loss of a proton will not affect the restoring forces in the O-O bond, i.e., will be solely a mass effect, the O-O frequency has been calculated for the Penney and Sutherland model for the ion, H-O-O^- (22), to compare with the value calculated for the H-O-O-H molecule (23), assuming an azimuthal angle of 90° for the molecule. The values obtained were 862 cm^{-1} for the ion and 846 cm^{-1} , a prediction of an increased frequency for the ion. The experimental values obtained (21) show the reverse effect, the ion having a frequency of 844 cm^{-1} , the molecule 877 cm^{-1} . This observed weakening of the bond would be predicted for the C_{2v} model on the basis that formation of the ion would destroy the symmetry and greatly weaken the resonance pictured for that molecule.

The superiority of the C_{2v} model over the C_2 structure is apparent not only in its explanation of the refraction and bond strength in the molecule, but also in the ease with which it accounts for the chemical properties of hydrogen peroxide.

Further comparison of these models will be made in connection with the interpretations of the dipole moment values measured in this research. It should be mentioned at this point that the C_2 model suggests the existence of

optical isomers while the C_{2v} form does not, and that demonstration of the non-existence of such isomers would very definitely favor the latter structure over the former.

Organic Peroxy Compounds

Several properties of organic peroxy compounds indicate that the linkages and their arrangement about the oxygens are the same for the -O-O- section of these substances as for the parent substance. The exaltation of refraction (24,25), for example, parallels that for hydrogen peroxide.

New structural features in close proximity to the peroxy group are present in some of the types of peroxy compounds and the effect of these on the nature of the bond as revealed by the molecular refractivity has been considered by Milas, Surgenor and Perry (25). The equality of the oxygen atoms of the peroxy group in this group of compounds has been debated just as for those atoms in hydrogen peroxide itself (26,27,28).

This dissertation will describe the measurements and interpretations of the dipole moments of five organoperoxides in benzene solution. Two of these have not been investigated in this way previously. In the discussions which follow, the moments will be considered in the light of four possible configurations, (a) the skew model,

(b) the folded structure, (c) the unbranched R-O-O-R' freely-rotating configuration, and (d) the branched model.

II. Experimental

Apparatus and Measurements

The apparatus and method of measurement were essentially those already developed in this Laboratory over a long period (29,30,31,32,33,4). The capacitance determinations of dielectric constant were made with a high-frequency bridge, the measuring cell being constructed of three concentric platinum cylinders and having a replaceable capacitance of about 177 micromicrofarads. The refractive indices were determined with a Pulfrich refractometer equipped with a specially designed cell to protect the sample from moisture in the air and to thermostat it (29). The density values were obtained with a pycnometer of 25 cc. volume.

The oscillator of the bridge was calibrated at seven frequencies covering the range 0.7 to 1.37 megacycles per second. The cell was calibrated by fillings with dry air and dry benzene. The capacity of the cell in each dielectric constant measurement was taken over the range of frequencies specified above in order that an extrapolation to zero frequency could be made to remove any residual inductance effects (30,31). Corrections for irregularities in the worm-drive of the precision measuring condenser of the bridge were applied to all the readings (31).

The pycnometer was calibrated with pure water and the density values were corrected for variations in ambient humidity and pressure and were reduced to in vacuo figures.

The thermostating bath used for all the measurements was of large size, filled with 50 gallons of transformer oil (General Electric Transil Oil). The dielectric constant of the oil was measured and found to be 2.221 at 30°C. The temperature regulation was within 0.01 to 0.02°C of the temperature used. The filling apparatus for all the measuring cells and pycnometer was constructed entirely of glass and was protected by drying tubes.

Methods of Calculation

The constant terms for the equations giving the dielectric constant, density and square of the refractive index of the solutions as linear functions of the mole fraction of the solute were adjusted by a least-squares routine (32,34) and checked graphically for validity in view of the possibility of association of solute molecules. Association, such as takes place with acetic or benzoic acid, would lead to non-linearity in these relations and would invalidate the procedures used here to calculate the dipole moments.

The Hedestrand formulation (35,33,4) was next applied in several cases to these data to obtain the infinite

dilution values of the molar refractivity MR_D and of the total polarization, P_{20} , but, in general, the Halverstadt and Kumler (36) formulation was used.

The dipole moments μ were then calculated by the equation

$$\mu = 0.01281 [(P_{20} - MR_D)T]^{1/2}$$

and are in Debye units (4).

A suggestion for the improvement of the values measured for substances of small dipole moments can be made here. The true differences in the precision condenser readings due to concentration changes in solutions of such substances may be less than the experimental error of the readings such as, for example, would be caused by absorption of moisture from the ambient atmosphere. This effect will be relatively great for dilute solutions.

In order to minimize the effect of slight contamination due to handling of the solutions and especially that due to unavoidable brief exposures to the air, it is suggested that the dielectric constant of the pure stock solvent be measured both before start of preparation of the solutions and at the end of the preparation, before the solutions are measured. Then, the effect of any small amount of moisture absorbed in handling the solvent and solution can be dealt with by introducing the mean of these two values of the dielectric constant of the solvent

into the least squares calculations as values of equal weight with the solution values of ϵ_{12} in the relation

$$\epsilon_{12} = a + bN_2$$

For the case of solvent alone $\epsilon_{12} = a = \epsilon_1$. Here ϵ stands for dielectric constant, N for mole fraction, the subscripts, 1 and 2, designating solvent and solute, respectively. Figure 16 shows some of the aspects of the problem.

The procedure just described has merit because (a) the accuracy of the individual capacitance measurements of the pure solvent is equal to that of the measurements of the solution, (b) the directly determined value of ϵ_1 has been checked in a way that cannot be applied to the solution values and it is used to orient the whole slope determination (see Figure 16), and (c) a direct check on the amount of contamination of the solutions by the highly polar water molecules is made in view of the fact that the pure solvent used in the final measurement will have had an exposure to the atmosphere at least equivalent to that of the last solution to be measured. If this safeguard reveals a dangerously high amount of contamination, then the solutions can be (and were in practice) discarded with a useful saving in effort and with avoidance of an otherwise hidden error.

This procedure with its emphasis on moisture contamination has the advantage of keeping this source of error in the mind of the experimenter at each stage of the work: in the design of the procedures and apparatus, in the course of the manipulations and measurements, and in the treatment of the experimental results. For example, a stream of dry air was used to protect the solutions during the opening of their containers and in making connections of the containers to transfer apparatus and positive pressures were maintained in the containers to prevent their breathing air.

Materials

Benzene. Thiophene-free benzene was stored above sodium and refluxed over sodium for several hours before use. It was then distilled with discard of first portions. The D-line refractive index and density were 1.4948 and 0.8676 gram per cc. at 30°C.

Di-t-butyl peroxide. A gift sample from the Shell Chemical Corporation was distilled at 98.5 mm. The fraction boiling at 52.5°C was used. This was the major part of the liquid. For it, $n_D = 1.3841$ at 30°.

t-Butyl hydroperoxide. This was purchased from the Lucidol Division of the Novadel-Agene Corporation. A fraction boiling at 51.8°C under 40 mm. was taken. This was

the large fraction, comprising most of the material, and had the D-line refraction, 1.3958 at 30°. A lower boiling fraction, 47-49.5° at 52 mm., was also taken for separate measurements to duplicate the material (45° at 40 mm.) used by Rogers and Campbell.

Dibenzoyl peroxide. Material of 99.5% purity was purchased from the Lucidol Division. It was recrystallized from chloroform by addition of methyl alcohol and was dried in a vacuum desiccator over drierite for two days.

Perlauric acid. Through the courtesy of Dr. Daniel Swern of the Eastern Regional Research Laboratory of the U. S. Department of Agriculture, a sample of this compound in an exceptionally high state of purity was obtained. This sample melted at 51.5 - 52° and had been prepared by Mr. W. E. Parker of that Laboratory. It was used as received.

Cumene hydroperoxide. A 20 gram sample of 98% cumene hydroperoxide in 62 grams of petroleum ether was received as a gift from the Hercules Powder Company through the courtesy of Dr. John H. Elliott. It was purified by a procedure kindly provided by R. W. Ivett and T. Marshall of that Company.

In this purification, about 41 grams of the petroleum ether solution of the peroxide was diluted to 150 cc. with benzene and added slowly to 25.8 grams of 40% aqueous sodium hydroxide cooled to 10°C. The addition was carried

out with vigorous stirring to keep the temperature below 20° . A precipitate of the sodium salt appeared as a white solid shortly after the start of the addition and the liquid became viscous, requiring the addition of benzene. When addition of hydroperoxide was complete, stirring was continued for fifteen more minutes and the suspension was filtered through sintered-glass filters. The filtrate was discarded.

The solid sodium salt was resuspended in 150 cc. of fresh benzene, stirring below 20° until all the lumps were broken up. The mixture was filtered again. This washing procedure was repeated four times in all. After the final filtration the solid was dissolved in a minimum amount of water cooled to 10° , and neutralized by passing carbon dioxide through the solution. When the solution became nearly neutral, benzene was added to dissolve the liberated hydroperoxide. This was removed and the aqueous phase was extracted twice more with benzene. All three benzene washes were combined and washed twice with distilled water to remove any inorganic salts. The benzene was distilled off at reduced pressure on a water bath. The recovered cumene hydroperoxide was analyzed by the method of Seubold and Vaughan (49) and showed a purity of 100.6% by this method. The high result is probably due to an inherent small error in the method of analysis.

III. Results

The results summarized below in tabular form give the quantities needed to calculate the polarization and refractivity by the Hedestrand (35) or by the Halverstadt and Kumler (36) procedures.

The equations and symbols for the Hedestrand procedure are:

$$\epsilon_{12} = a + bN_2$$

$$d_{12} = c + dN_2$$

$$n_{D12}^2 = e + fN_2$$

The constants a , c , e will be recognized as the pure solvent values of the dielectric constant, density and square of the D-line refractive index as obtained by least-squares treatment of the measured values of those properties for the solvent and the solutions. At the same time, b , d and f are the slope values in the linear relation between the solution values of those same properties and the mole fraction of the solute, also obtained by the least-squares routine. The molar polarization P_{20} of the solute at infinite dilution and the molar refractivity MR_D of the solute obtained by the Hedestrand formulation from these values, together with the dipole moment in debyes as obtained from the polarization and refractivity, are also tabulated.

Where the Halverstadt and Kumler method of calculation was used another set of symbols applies:

$$\begin{aligned}\epsilon_{12} &= a + gw_2 \\ v_{12} &= h + jw_2 \\ n_{D12}^2 &= e + kw_2\end{aligned}$$

Here we show the weight fraction w_2 instead of mole fraction for the solute and specific volume v_{12} instead of density for the solution. The Halverstadt and Kumler method is somewhat simpler than the Hedestrand method.

Table I

The moment of di-t-butyl peroxide in benzene

Temp.	a	b	c	d	e	f	P ₂₀	MR _D	μ^a
30	2.2628	0.376	0.8674	-0.173	-	-	60.86	43.1	0.94
Temp.	a	g	h	j	e	k	P ₂₀	MR _D	
30	2.2629	0.305	1.15299	0.056	2.2353	-.303	60.86	43.1	0.94
50	2.2231	0.2015	1.18180	0.1069	-	-	60.05	43.1	0.95

a. Rogers and Campbell found $\mu = 0.92$ at 25°C in benzene, their P₂₀ and MR_D values being 60.78 and 43.44.

Table II

The moment of t-butyl hydroperoxide in benzene

Temp.	b.p.	a	ϵ	h	j	e	k	P ₂₀	MR _D	μ^a
30	51.8 (40 mm.)	2.2622	3.46	1.15162	0.0483	2.2349	-0.373	91.1	24.4	1.82
30	47-49.5 (52 mm.)	2.2630	3.604	-	-	-	-	93.7	"	1.86
50	51.8 (40 mm.)	2.2220	2.984	1.18071	0.0326	-	-	85.1	"	1.79
50	51.8 (40 mm.)	2.2193	3.060	-	-	-	-	86.5	"	1.81

a. Rogers and Campbell found = 1.87 at 25°C in benzene,
their P₂₀ and MR_D values being 95.80 and 24.52.

Table III

The moment of cumene hydroperoxide in benzene at 30°C

a	g	h	j	e	k	P ₂₀	M _{R_D}	μ
2.2630	2.1717	1.15296	-.19412	2.2327	0.04924	106.14	43.95	1.76
2.2625	2.302	1.15300	-.19237	-	-	109.91	43.95	1.81

Table IV

The moment of dibenzoyl peroxide in benzene at 30°C

a	b	c	d	e	f	P ₂₀	MR _D	μ^a
2.2627	3.707	0.86733	0.8127	2.2320	0.53	112.85	64.70	1.55

a. Oesper and Smyth obtained the value = 1.58
at 45°C in benzene, their P₂₀ and MR_D being
110 and 63.

Table V

The moment of perlauric acid in benzene

Temp.	a	b	h	j	e	k	F ₂₀	MR _D	μ
30	2.26241	2.28532	1.15270	-.04674	2.2355 (mean of two det.)	-.223	164.95	61.342 (theoret.) 60.5 (obs.)	2.27 2.28
50	2.2231	2.2267	1.18166	-.06143	-	-	165.92	61.342 (theoret.) 60.5 (obs.)	2.35 2.36

IV. Discussion

It should be noted in the discussions of the observed moments in relation to the several models of the peroxy structure that the individual bond moments expected will vary from structure to structure.

For the model I we will use the Rogers and Campbell (7) values, 1.71D for the $H \rightarrow O$ moment, and 0.62 for the $C \rightarrow O$ moment. It is also appropriate to follow their choice of $\varphi = 100^\circ$ and $\theta = 105^\circ$ where the size of the attached groups does not rule otherwise (7).

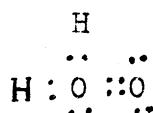
For the model III the $H \rightarrow O$ moment should be 1.66D with our choice of azimuthal angle (100°) and the Linton and Maas (5) value of μ (2.13) for hydrogen peroxide. The $C \rightarrow O$ moment should be 0.62D based on the moment of di-n-propyl ether by the same reasoning as used for the C_2 model (7).

For the free-rotation model it can be shown that the resultant moment is the same as for a fixed skew-structure with $\varphi = 90^\circ$ which would give the $H \rightarrow O$ moment as 1.56D on the basis of the observed hydrogen peroxide moment. But the absence of free rotation in hydrogen peroxide as evidenced by its Raman and infrared spectra (10) rules out this choice and we shall turn to the 1.71D value of the C_2 model for assignment to the $H \rightarrow O$

bond where free rotation may be thought to be a possibility. This somewhat shaky basis of choice turns out to cause no difficulty in the one case in which it has importance.

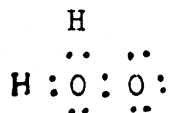
The branched structure causes real difficulty in the assignment of bond moments. Uncertainty concerning the nature of the O-O bond in this molecule makes it truly difficult to partition the hydrogen peroxide moment into $H \rightarrow O$ and O-O moments.

The structure



would probably have a moment lower than 2.13D, there being no great separation of charge and its moment would probably be close to that of water, 1.84D. In any case this structure is improbable due to the fact that there is no evidence that oxygen can expand its valence shell to ten electrons.

The structure



contains a dative bond between the oxygen atoms which might be expected to be highly polar and to be disposed in the sense of the combined $H \rightarrow O$ bond moments. Assuming any reasonable H-O-H angle, the variance of the

angle χ between the O-O bond and the bisector of the H-O-H angle (see Fig. 1, IIb) will have a large effect on the moment of the molecule, and hence on the value assigned to the O \rightarrow O moment. For example, taking the water value for the H \rightarrow O moment, 1.51, the H-O-H angle as 100° and χ as 90° , the O \rightarrow O moment would be 0.88D, which appears too low for a semipolar bond (37).

Decrease in χ would give a higher value to the O \rightarrow O moment as also would widening the H-O-H angle, but these changes cannot be independent of each other because they would not account for the sharp decrease in moment in the series hydrogen peroxide, t-butyl hydroperoxide and di-t-butyl peroxide.

Rather, it would appear that of the parameters involved, the χ value and the valency angle might vary from peroxide to peroxide. The possibility of the existence of the branched arrangement of the peroxy group appears remote at this stage, but a re-evaluation may be possible when a greater number of simple peroxides and hydroperoxides have been studied. In the re-evaluation, an adjustment of these parameters in a systematic way may produce some evidence for this structure. From the moment values available, viz., those for hydrogen peroxide, t-butyl hydroperoxide and di-t-butyl peroxide, we have attempted a limited adjustment of the bond angle

and the $O \rightarrow O$ moment, keeping χ at 90° , $H \rightarrow O$ at 1.51D, and $R \rightarrow O$ at 1.02D. The results are fairly reasonable for the bond angles: $90^\circ 35'$ for the hydroperoxide and hydrogen peroxide and $125^\circ 55'$ for the di-t-butyl peroxide only when $O \rightarrow O$ is 0.15D, but this moment is surely too low.

The investigators who have used other methods such as infrared and Raman spectroscopy favor the C_2 model because it accounts for the Raman lines reported by Venkateswaran (38) and by Simon and Feher (39, see also 40,12,41,42,43). The C_{2v} model accounts for these lines also. In any case, not all the frequencies have been conclusively identified for the C_2 model and the assignments have not been made for all the observed bands (12,43). The C_2 structure has covalent single bonds and Giguere and Schomaker (44) undertook investigation of the hydrogen peroxide molecule by electron diffraction in order to determine the oxygen-oxygen covalent single bond length. The X-ray investigation made by Lu, Hughes and Giguere (45) on the addition compound of urea and hydrogen peroxide gave the azimuthal angle as 106° . The value obtained by Abrahams, Collin and Lipscomb (46) for hydrogen peroxide itself by X-ray diffraction was 94° . They also found the bond angle $H-O-O$ was 97° .

Di-t-butyl peroxide

As the results in Table I show, the measurements at 30° and 50°C give practically the same value for the dipole moment of di-t-butyl peroxide, 0.94 and 0.95D, respectively. This might mean that there is no change in the rigidity of the molecule in the form with a C_2 point-group symmetry in this range of temperature. At first glance an alternate explanation might appear to be that rotation to the full extent possible has already set in at 30°, because as is shown by the Fisher-Taylor-Hirschfelder atomic models there can be no possibility for completely free rotation about the O-O axis. Only an angle of 120° is open to rotation, or, more correctly, "libration." This alternate explanation is ruled out, however, because the moment for such free libration would be only 0.58D, and our data fit the rigid structure, showing no free rotation or libration.

This rigid Penney and Sutherland structure (the C_2 structure) according to the F-T-H models can have an azimuthal angle, φ , no smaller than 118° for di-t-butyl peroxide. In this set of models, the oxygen atoms are cut for a valency angle of 110°, whereas in our earlier discussions, following Rogers and Campbell, we have taken it to be 105°, which would force the azimuthal angle to a greater value. The dipole moment for di-t-butyl

peroxide with $\theta = 105^\circ$, $\varphi = 120^\circ$, the $C \rightarrow O$ moment 0.62D and the $(CH_3)_3C-$ moment 0.4D will be 0.99D (see Figure 8) which is not greatly different from our measured value.

For the C_{2v} structure, if φ is taken as 125° and the bond moments are taken the same as discussed earlier, the predicted moment would be 0.94D. We do not imply that this figure favors the C_{2v} structure over the C_2 structure, because the value $\varphi = 125^\circ$ is probably too low for the C_{2v} structure. On the other hand, while use of more correct values of φ would give predicted moments in better agreement between the experimental values and the C_2 model, we point out that more correct values of the $C \rightarrow O$ bond moment would bring the C_{2v} model into better agreement with the experimental value and C_2 into poorer agreement: so that in the net, we must conclude that we cannot favor either one of the two models over the other. To explain the better choice of the $C \rightarrow O$ moment value, we point out that it is probably greater than 0.62D by an amount proportional to the increase in the $H \rightarrow O$ moment in hydrogen peroxide over its moment in water (1.71 to 1.51 in one case, 1.66 to 1.51 in the other).

The plots of P_2N_2 against N_2 for our measurements of this substance were good straight lines and passed

through the origin, indicating that in the concentration range we used there is no association of the di-*t*-butyl peroxide in benzene (47). These Hoecker plots are shown in Figure 3.

t-Butyl hydroperoxide

Using the 30° and 50° values determined for the main fraction (51.8° at 40 mm.) we take 1.81D as the experimental value of the electric dipole moment for *t*-butyl hydroperoxide. The much smaller fraction which corresponds to the fraction used by Rogers and Campbell (7) gives a higher moment in agreement with their value. This fraction is certainly not pure *t*-butyl hydroperoxide and we reject their value, 1.87D, for the moment.

As for di-*t*-butyl peroxide, the Hoecker plots, here shown as Figure 4, are linear and pass through the origin as required for a non-associated solute.

For a rigid skew structure with $\varphi = 100^\circ$, $\theta = 105^\circ$, $H \rightarrow O = 1.71D$, $C \rightarrow O = 0.62D$, and $(CH_3)_3C = 0.4D$, the moment is 1.78 as shown in Figure 9 (see also reference 7). Almost the same value 1.79D results for the structure III (see Figure 11) using the same azimuthal angle and moments as for the structure I, except that $H \rightarrow O$ is taken as 1.66D as discussed earlier.

The agreement of the I (Fig. 1) and III (Fig. 2) structures with the experimental value is good in both cases in view of the uncertainty in the values of the parameters used. The best evidence in favor of the I as opposed to the III form would be the separation of the hydroperoxide into optically active forms. It is interesting to note that in the case of the hydroperoxide, but not for the symmetric peroxides or hydrogen peroxide, the branched structure IIb in Figure 1 should be resolvable into optical isomers.

From consideration of the dipole moment data together with the bulk of the groups, one would conclude that the C-O links do not rotate fully about the O-O axis in t-butyl hydroperoxide, as shown in Fig. 11 completely-free rotation would result in a moment of 1.93D. This calculation assumes, contrary to fact, that no steric effects are present. The F-T-H models show that only with the help of an improbable, closely-synchronized motion of the methyl groups within the butyl group can the hydrogen atom at the other end of the O-O axis be rotated about that axis without touching upon the spheres of repulsion about the methyl hydrogens, and even in this case the clearance is very small. In view of the probable motions of the methyl

groups a restricted libration would result, and we note that this would predict a moment smaller than the experimental value, 1.81D. It turns out that the dipole moment data for this molecule do not provide a means of distinguishing sharply between a completely rigid structure and one with a large oscillation of the linkages attached to the O-O axis. In this situation we turn back to the finding for the di-t-butyl peroxide molecule that the structure is rigid to say that in all probability the same behavior is shown for this closely related molecule, t-butyl hydroperoxide.

Cumene hydroperoxide

The mean of the two observed values, 1.76 and 1.81D, is 1.78D. The Hoecker plots (see Figure 5) are truly linear and pass through the origin.

Prediction of the moment from assigned values of the moments of the constituent bonds in this molecule must take into account the C_6H_5-C moment and the

rotation of the $C_6H_5-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}$ group about the C-O axis.

This is difficult in view of the present uncertainty about the value to ascribe to the C_6H_5-C moment. Figures 9,10,11 and 12 show that, assuming complete

rotation of the phenyl and methyl groups about the C-O axis, only a small range of values can be assigned to the $\text{C}_6\text{H}_5 \rightarrow \text{C}$ moment in order to bring the moment for the molecule lower than the moment for t-butyl hydroperoxide as calculated. On either side of this small range, the resultant moment of the molecule will be greater than for t-butyl hydroperoxide. To minimize the moment of cumene hydroperoxide, the moment of the $\text{C}_6\text{H}_5 \rightarrow \text{C}$ bond turns out to be about 0.15D (as based on structure III) and this gives a value of 1.77D for the moment of the molecule in good agreement with the observed value. This assignment of 0.15D to the $\text{C}_6\text{H}_5 \rightarrow \text{C}$ moment is tantamount to an assignment of the same value to the $\text{H} \rightarrow \text{C}$ moment for an aromatic C-H link. The whole calculation is based on the usual assignment of 0.4D to the $\text{CH}_3 \rightarrow \text{C}$ bond moment and the assignment of 0.62D to the $\text{C} \rightarrow \text{O}$ moment. In an effort to check this calculation by application to other molecules where the same substitution of C_6H_5 for CH_3 is present, we did not find a sufficient amount of accurate dipole moment data available.

Perlauric acid

The observed moment for this compound is 2.28D at 30°C and 2.36D at 50°C. The Hoecker plot was made for

the 30°C data (see Figure 7) and is a straight line through the origin. To investigate possible effect of decomposition of the perlauric acid taking place at the higher temperature, the dielectric constant of the solutions measured at 50° were remeasured later at 30°C and found the same as the original measurements at 30°C.

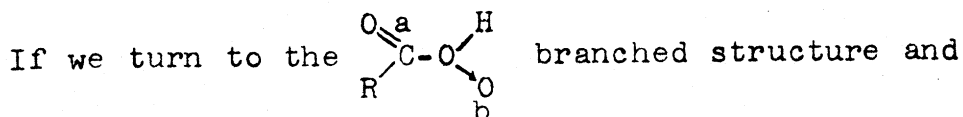
The observed values are much lower than predicted for either the model I (2.96D) and for the structure

$$\text{C}_{11}\text{H}_{23}\overset{\text{O}}{\parallel}\text{C}-\text{O}-\text{O}-\text{H}$$

with free rotation about the O-O axis (~3 D). The structure proposed by Giguère and Olmos (48) for peroxycarboxylic acids (see Figure 13) should be considered in view of their strong evidence for intramolecular hydrogen bonding in such acids. They investigated the spectra of performic and peracetic acid and came to the conclusion that these peracids contain chelate structures of planar or slightly puckered configurations. They suggest that the electrostatic attraction of the carbonyl oxygen for the hydrogen atom is sufficient to overcome most if not all of the potential barrier (4-5 kcal per mole) restricting rotation about the O-O bond.

As shown in Figure 13, the H-O-O- angle is 100°, a value 5° lower than that in hydrogen peroxide to account for the replacement of a hydrogen atom by an

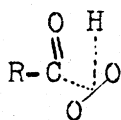
electronegative group (48). They think that their estimate may be conservative for this effect. This model gives 1.76D for perlauric acid. If we assume another 5° narrowing of the H-O-O angle and that the ring is puckered even for an azimuthal angle of 30° , the resultant dipole moment is heightened to 2.05D but remains far lower than the observed value. Better agreement with experiment would result if the $C \rightarrow O$ moment were taken greater than 0.62D.



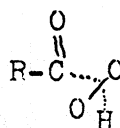
assign a value of 100° to the H-O-O angle and a value of 0.29D to the $O \rightarrow O$ bond moment, we get a value of ~ 3 D for the molecule on the assumption of free-rotation about the C-O bond and coplanarity for the C-O, O-H and O-O bonds. If a branched skew structure (IIb; Figure 1) is present as discussed earlier for the branched model a larger moment would result from free rotation, but for this structure greater proximity of the carbonyl oxygen (a) to either the b oxygen atom or the hydrogen atom will hinder rotation and lower the moment to a value closer to the observed value.

For the structure III, the average moment for rotation around the C-O axis would be 2.91D. The inter-

action of the carbonyl oxygen with the other oxygens and with hydrogen should be taken into account in the rotation. The moment values for the limiting cis- and trans- arrangements

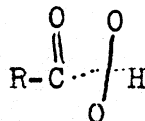


cis



trans

would be 1.07 and 3.97, respectively, the cis position should be favored over the trans position due to the attractive forces between the hydrogen atom and the carbonyl oxygen in the cis arrangement. The "gauche" arrangements in which the carbonyl oxygen is in closest proximity to either of the other oxygen atoms



gauche form

would not be favored for it would cause a repulsion between the oxygen atoms. It is possible therefore to have a moment resulting from the model III which would be close to the experimental one. Increase in temperature would also be expected to raise the moment as observed since the rotation would be able more readily to surmount the barriers indicated at the several stages of rotation.

Dibenzoyl peroxide

Apparently, the moment of this molecule is little affected by temperature. Our value at 30°C, 1.55D, is little different from the value 1.58D obtained at 45°C in the same solvent, benzene, by Oesper and Smyth (6). It is obvious that in the absence of special effects all of our guiding models, the III, I, free-rotation and branched models, would predict a higher value than that observed. The nature of the factors producing the observed value will be better disclosed after study of related substances, such as perbenzoic acid, t-butyl perbenzoate and diacetyl peroxide, have been made.

The Hoecker plot for dibenzoyl peroxide was also linear and passed through the origin (Figure 6).

V. Summary

The electric dipole moments of di-*t*-butyl peroxide, *t*-butyl hydroperoxide, cumene hydroperoxide, perlauric acid and dibenzoyl peroxide have been measured in benzene at 30°C. The moments of the di-*t*-butyl peroxide, *t*-butyl hydroperoxide and perlauric acid were also measured at 50°C. These measurements represent the first reported values for cumene hydroperoxide and perlauric acid.

The measured moments have been discussed in relation to four principal structural configurations, viz., the Penney and Sutherland rigid skew-structure I which has a C_2 point-group symmetry in the parent substance (H_2O_2), a freely rotating structure which at any instant has a C_2 point-group symmetry in H_2O_2 , a branched structure containing an $O \rightarrow O$ semipolar bond IIa and IIb, and a model III original with this dissertation and which has a C_{2v} point-group symmetry in H_2O_2 .

For di-*t*-butyl peroxide, *t*-butyl hydroxide and cumene hydroperoxide the observed moments support about equally the I and III models and indicate that practically no rotation of the linkages about the O-O axis takes place. It is noted that a choice between these two structures could be made by isolation of optical isomers for these molecules, the skew model predicting their

existence, the model III ruling them out. In the case of cumene hydroperoxide the assignment of bond moments brings into discussion the moment of an aromatic C-H link and the calculations lead to an assignment of the value 0.15D to that linkage.

Perlauric acid shows a moment which may be explained with only moderate success about equally well with the III and IIb structures and with a chelated structure proposed by Giguere and Olmos for peracids.

The moment for dibenzoyl peroxide appears to be very little affected by temperature and this may indicate that its structure is rigid. Any further interpretations of the moment value must await measurements on related compounds.

The dependency of the polarization on concentration was studied in this work and has shown that the molecules of the solute peroxide are not associated at the studied concentrations.

An improved procedure has been demonstrated for the determinations and calculations in dealing with small dipole moments.

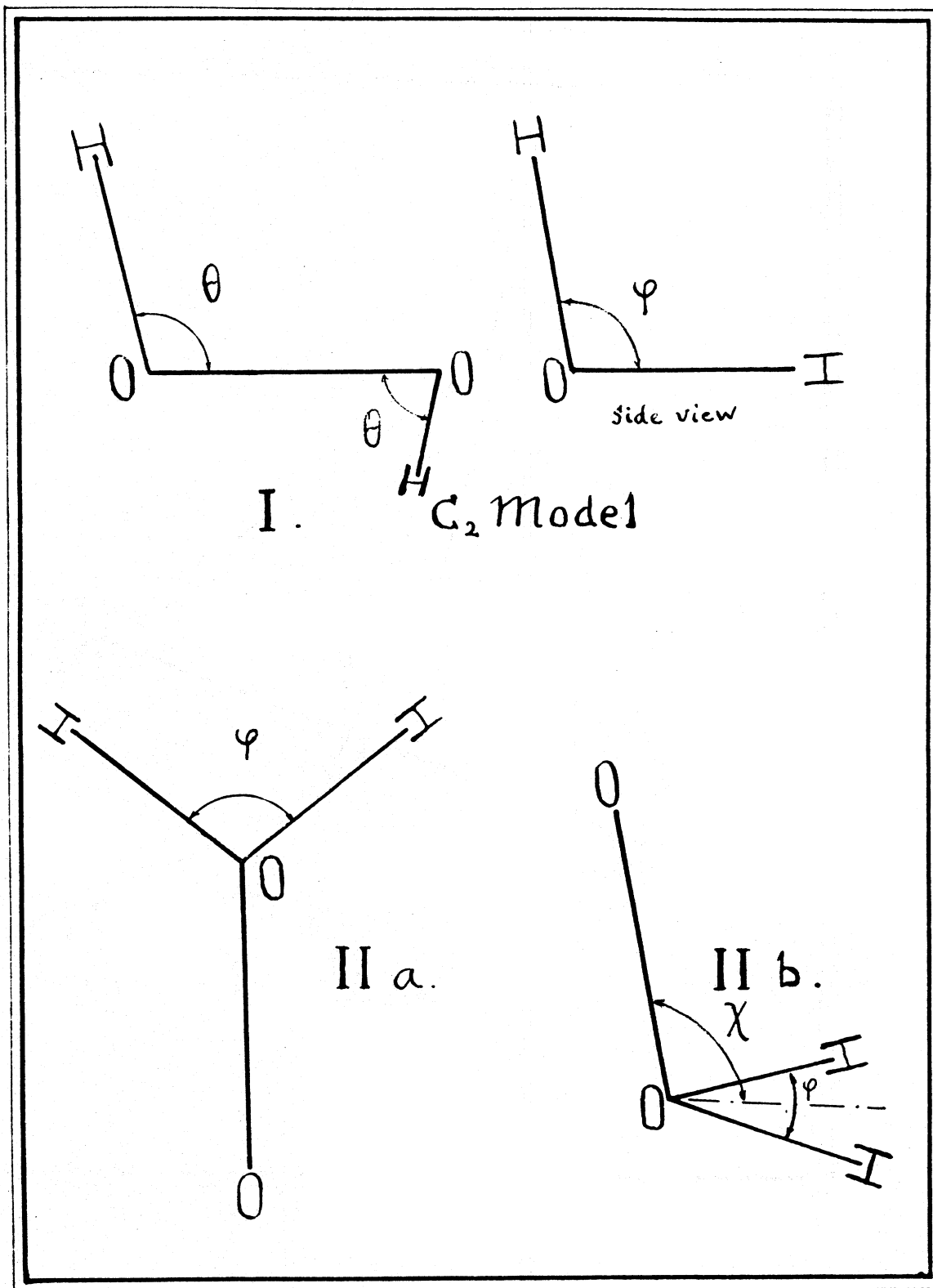


Fig. 1.

C_{2v} Model.

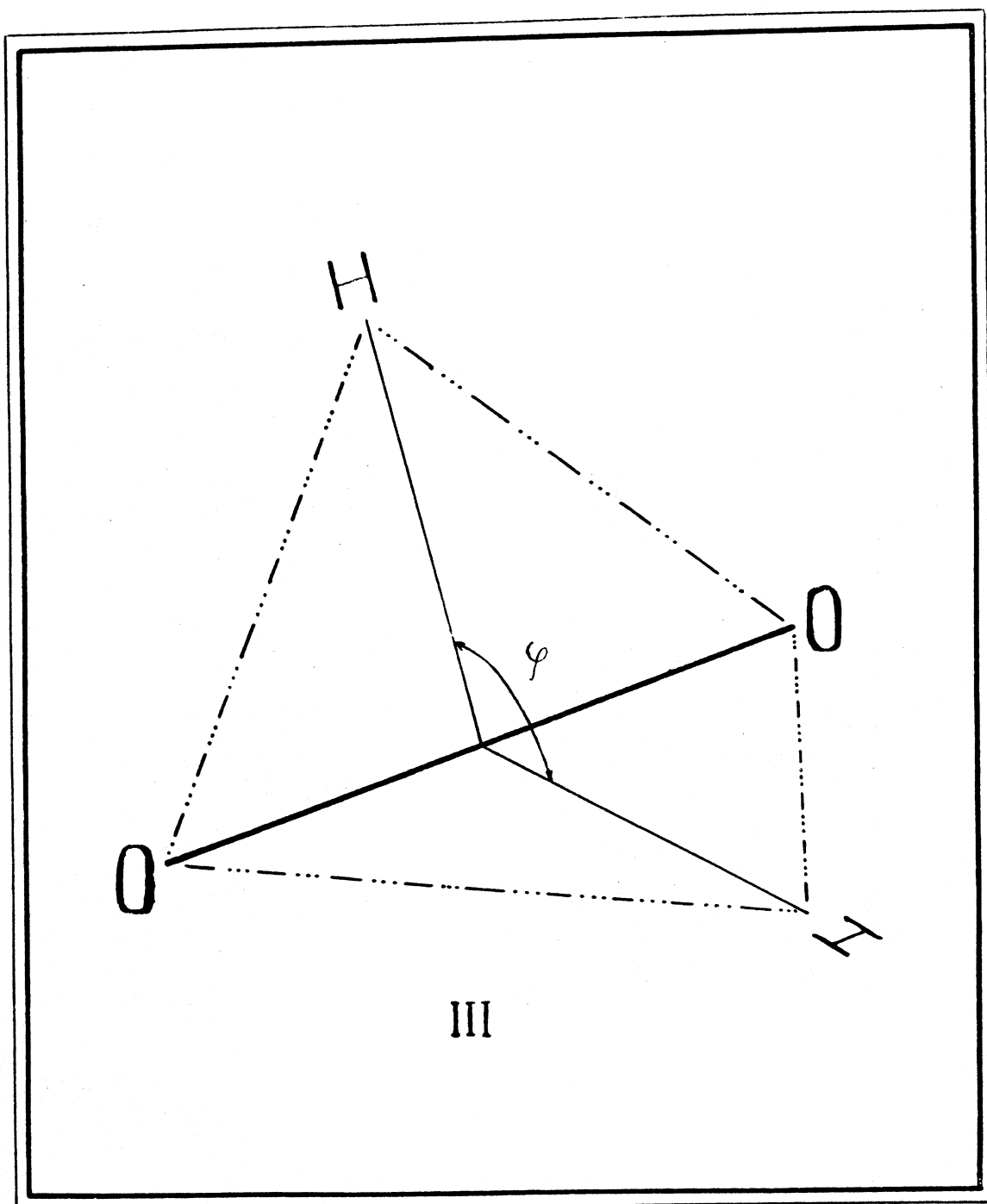


Fig. 2.

Di-*t*-butyl peroxide.

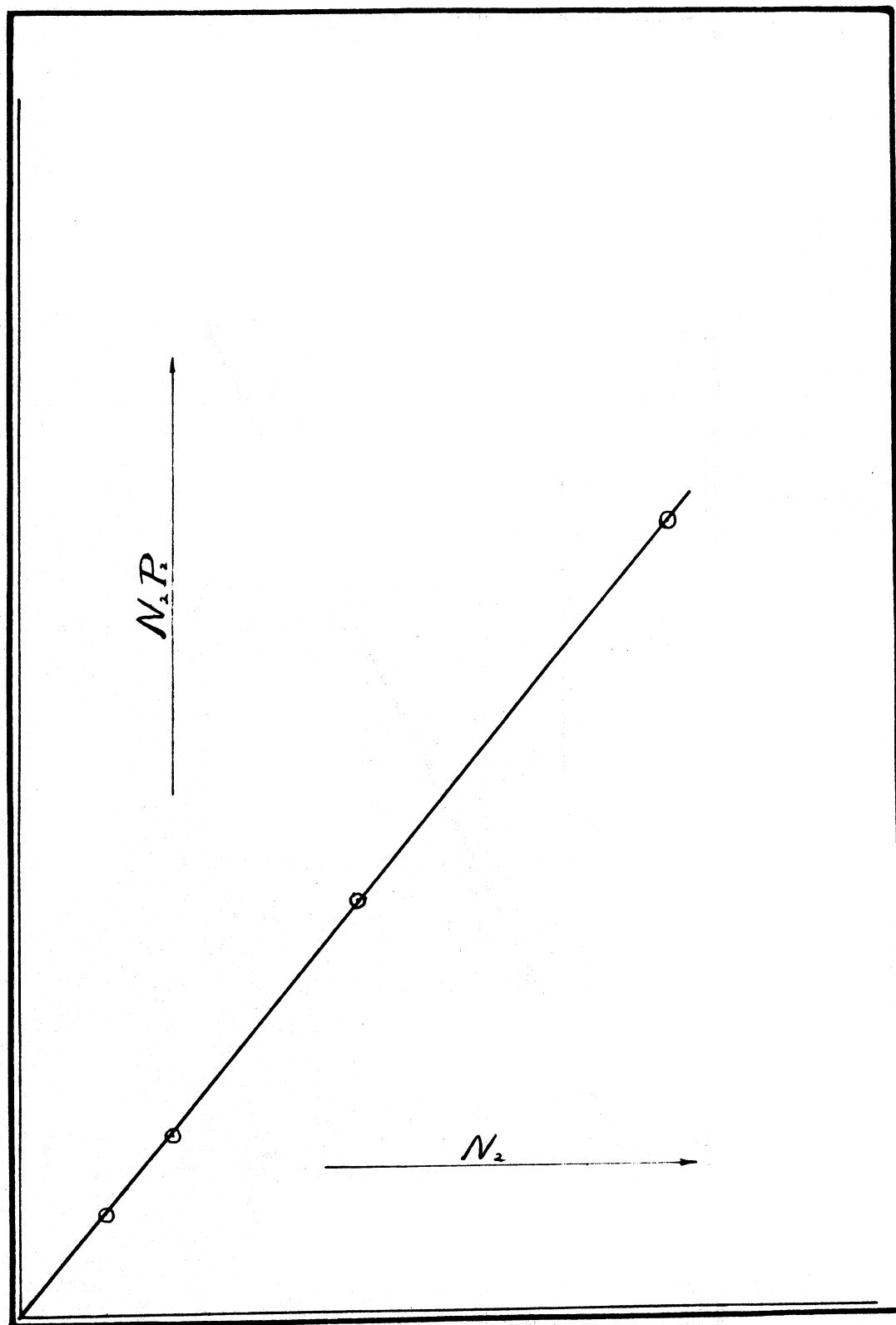


Fig. 3.

t-Butyl hydroperoxide.

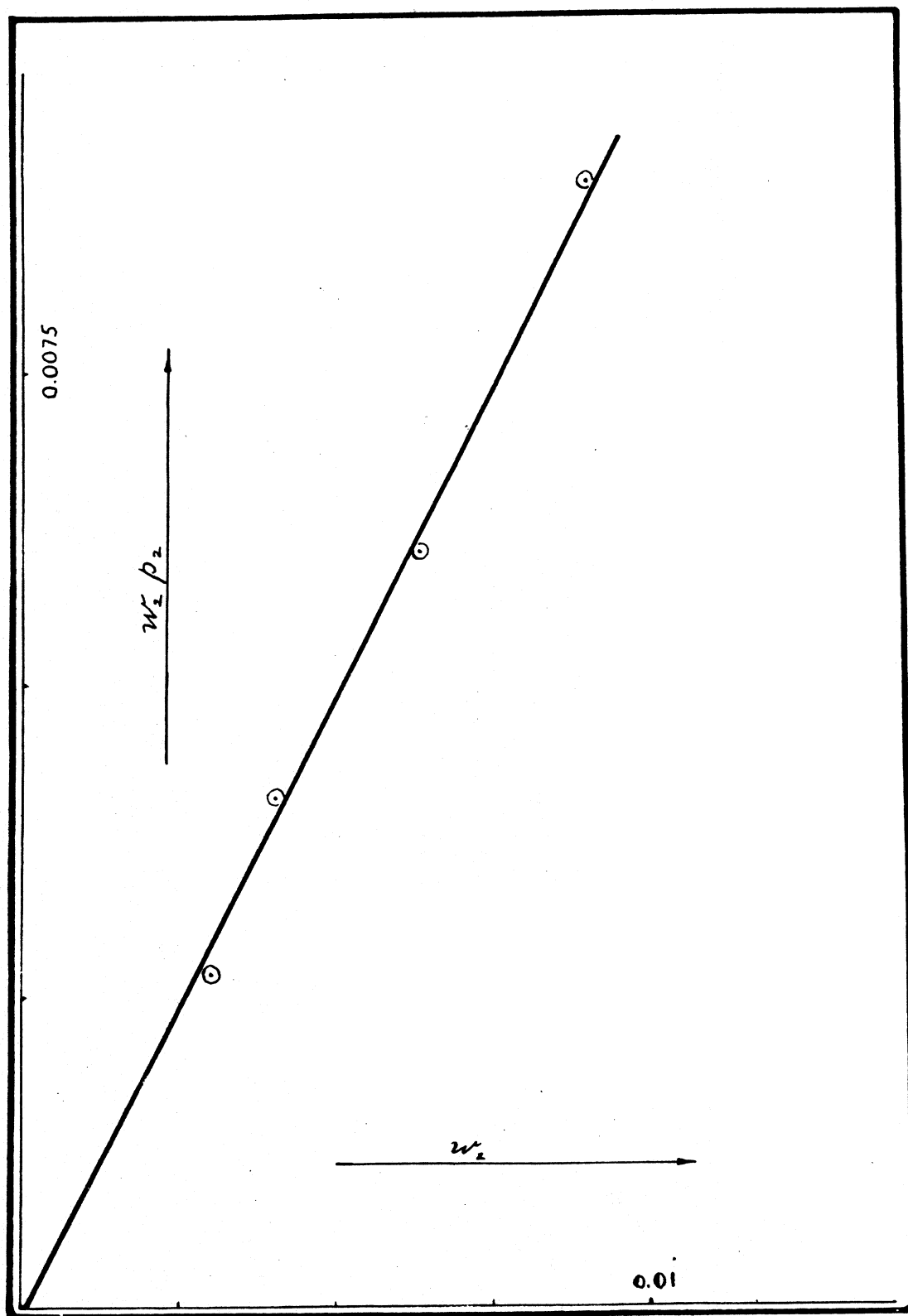


Fig. 4.

Cumene hydroperoxide.

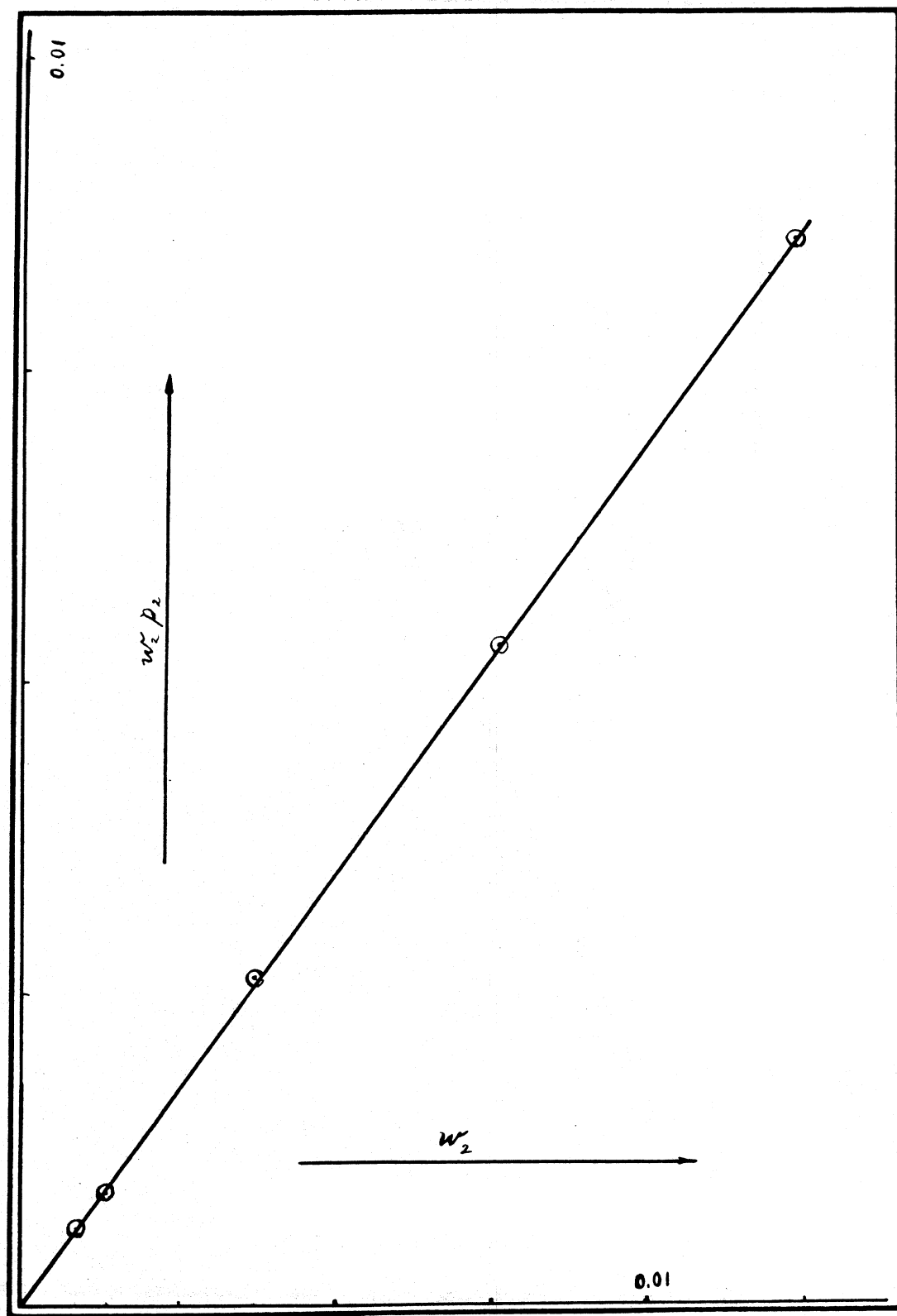


Fig. 5.

Di-benzoyl peroxide

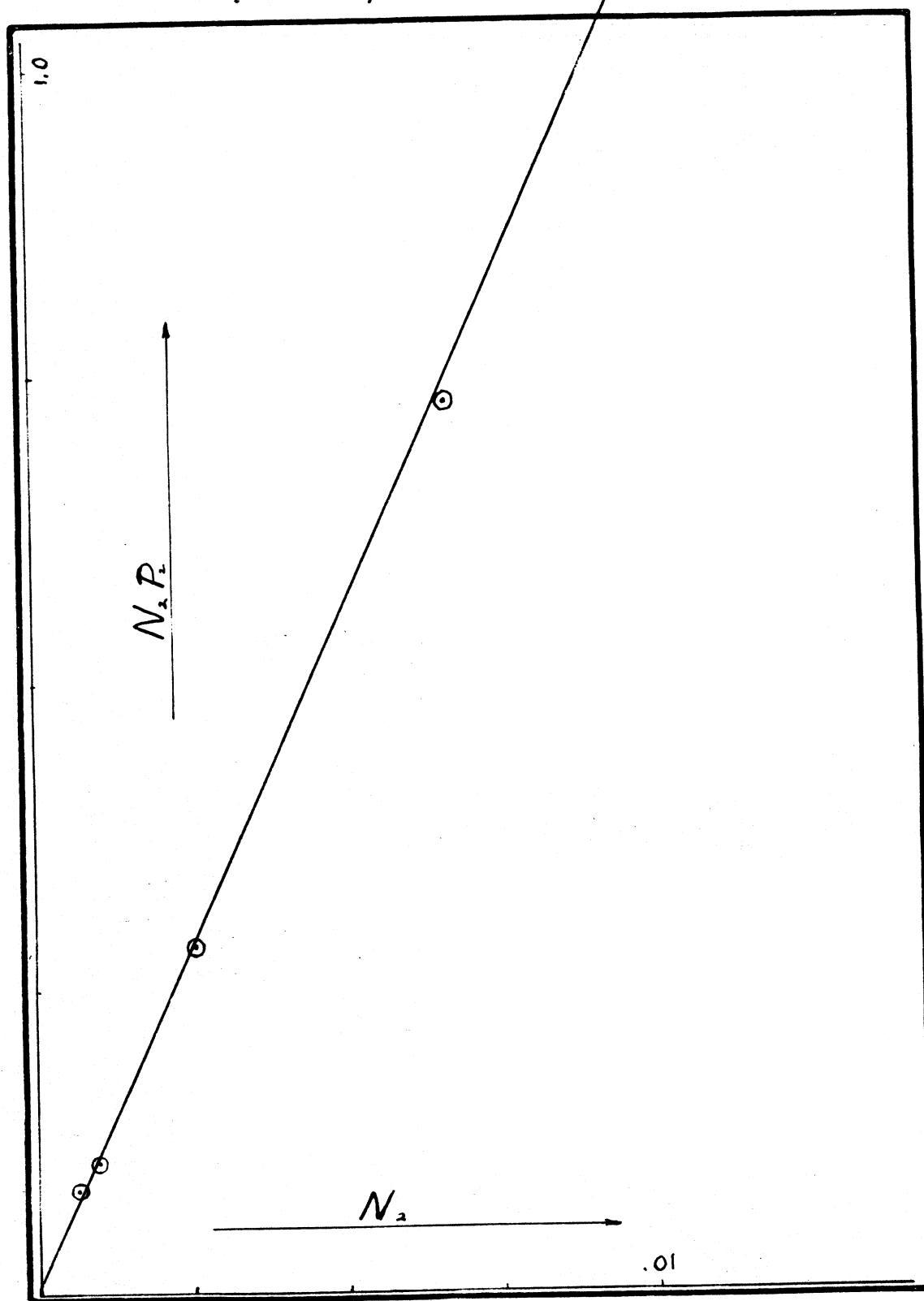


Fig. 6.

Perlauric acid.

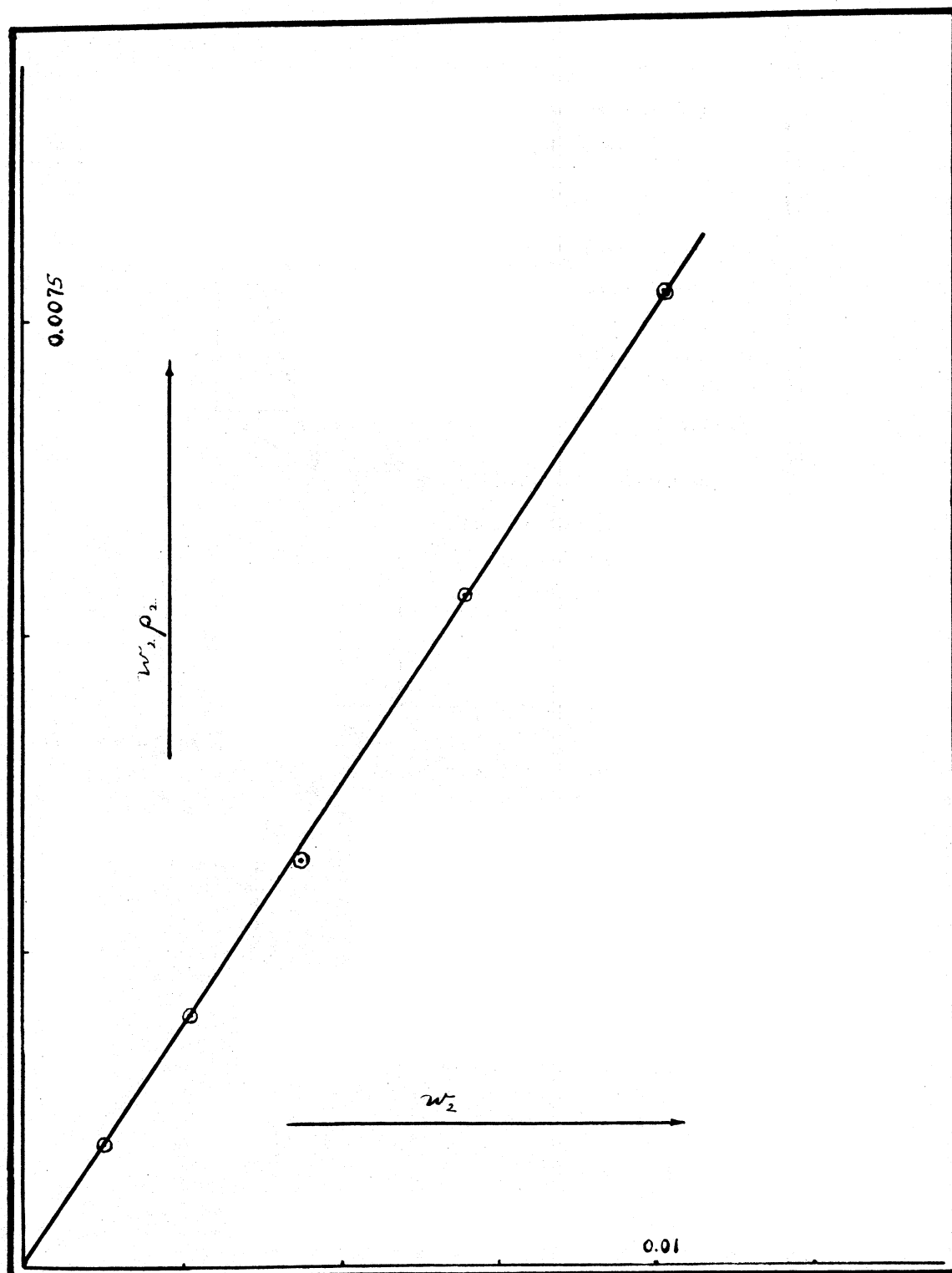


Fig. 7.

Di-*t*-butyl peroxide. Dipole moment
for C_2 model.

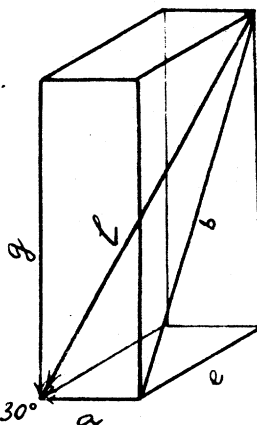
$$\mu^2 = (b-e)^2 + g^2$$

$$\mu \approx .99 D.$$

ℓ is the sum of vectors
for $M_{C_{10}}$ and $M_{(C_{10})_{10}}$

$$\ell = 0.62 + 0.4 = 1.02 D.$$

a, b, e and g are
perpendicular or
parallel to each other
addenda into which
both of ℓ vectors are
divided.



$$e = b \sin 30^\circ = 1.02 \cos 15^\circ \sin 30^\circ$$

$$b = 1.02 \cos 15^\circ \approx .9853$$

$$g = b \cos 30^\circ \approx .8533$$

$$e \approx .4926$$

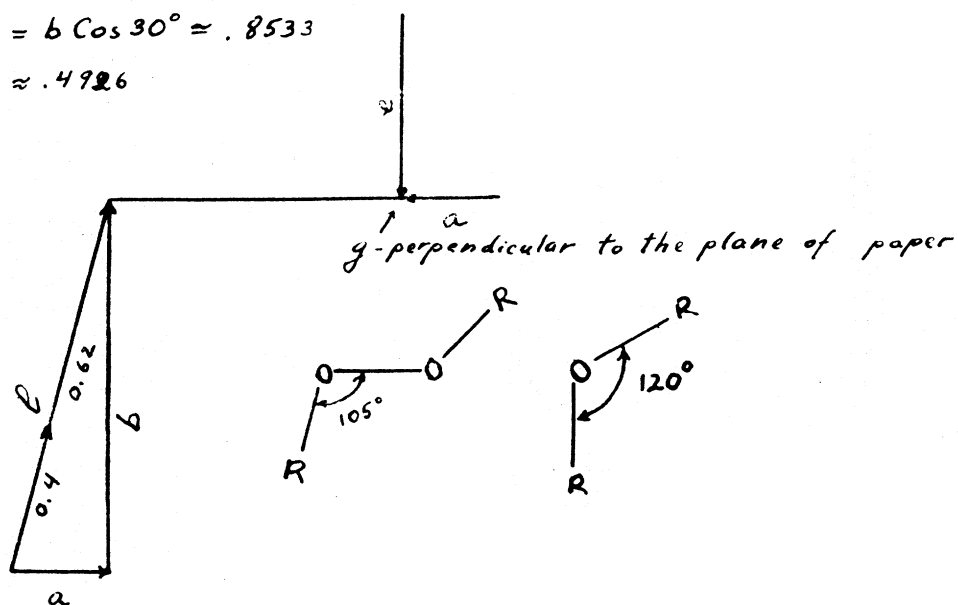


Fig. 8.

t-Butyl hydroperoxide. Dipole moment
for skew structure.

$$\mu^2 = (b-p)^2 + (f-a)^2 + h^2$$

$$\underline{\mu = 1.78 \text{ D.}}$$

a and b same as in Fig. 8.

$$p = 1.71 \cos 15^\circ \sin 10^\circ = .2868$$

$$f = 1.71 \sin 15^\circ = .4426$$

$$h = 1.71 \cos 15^\circ \cos 10^\circ = 1.6267$$

1.71 is value for $M_{H=0}$.

For meaning of p , f and h compare
this Fig. with Fig. 8. ($1.71^2 = h^2 + p^2 + f^2$)

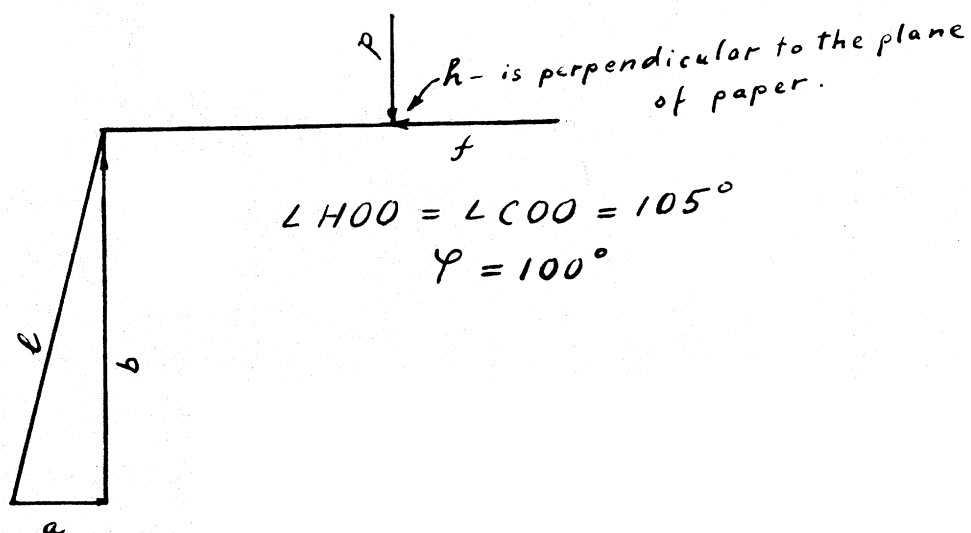


Fig. 9.

Cumene hydroperoxide. Dipole moment for skew structure.

The moment of H-O
is divided here in f' and p'
which are parallel or
perpendicular to K and r
in their mean positions.

$$\mu^2 = (K + .62 - p')^2 + (h^2 + f'^2) + r^2$$

When $\alpha = .18^\circ$

$$\mu = 1.76 D.$$

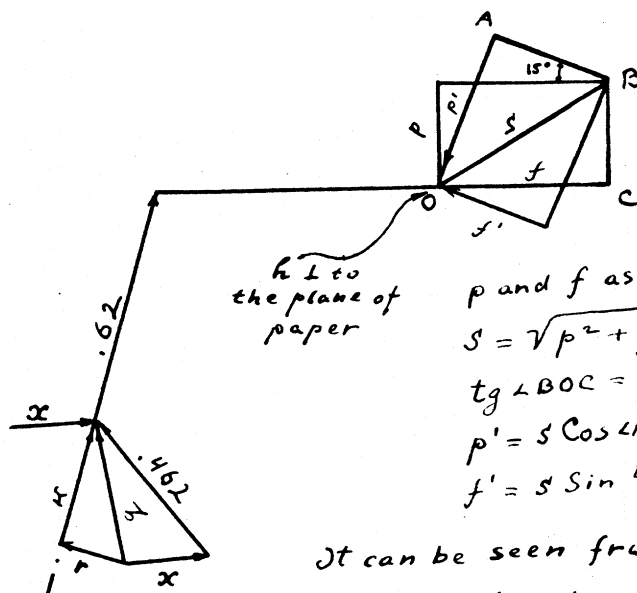
$$C_6H_5 \rightarrow C \text{ moment} = \alpha$$

$$CH_3 \rightarrow C \text{ moment} = .462$$

$$\vec{q} = \vec{\alpha} + .462$$

$$\vec{q} = \vec{K} + \vec{r} \text{ and } q^2 = K^2 + r^2$$

$r \perp K$ and r rotates around K as an axis.



p and f as in Fig. 9.

$$S = \sqrt{p^2 + f^2} = .52642$$

$$\tan \angle BOC = .64807 \quad (\angle BOC = 33^\circ)$$

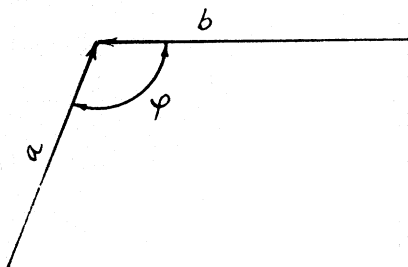
$$p' = S \cos \angle AOB = S \cos 42^\circ = .3912$$

$$f' = S \sin 42^\circ = .35224$$

It can be seen from the nature
of eq. that only a small range
for values of α will make the
total dipole moment for cumene hydroperoxide
lower than that for *t*-butyl hydroperoxide.
"Negative" α will make the moment larger.
Minimum value comes when $z^2 + (K + .62 - p')^2$ is min.

Fig. 10.

Dipole moment values.



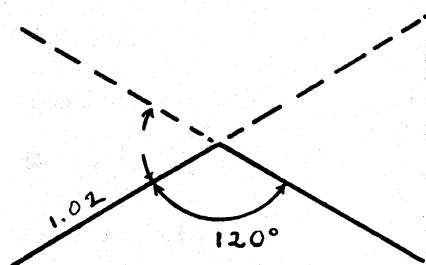
μ for di-*t*-butyl peroxide and for *t*-butyl hydroperoxide based on C_{2v} model for hydrogen peroxide.

$$\mu^2 = a^2 + b^2 + 2ab \cos \varphi$$

φ for first compound is not known. Experm. value .94D requires $\varphi \approx 125^\circ$

$$\begin{aligned} \mu_{t\text{-butyl hydroperoxide}} &= \\ &= 1.71^2 + 1.02^2 + 2 \times 1.71 \times 1.02 \cos 100^\circ \\ &= \underline{1.79 \text{ D}} \end{aligned}$$

Free rotation value for *t*-butyl hydroperoxide,
 $\underline{R-O-O-H} \cdot \mu = \sqrt{(1.02^2 + 1.71^2) \cos^2(105^\circ - 90^\circ)} = \underline{1.93 \text{ D}}$



\cdots and \wedge are limiting positions for the libration of groups around O-O axis in di-*t*-butyl peroxide

$$\overline{\mu^2} = \frac{(2 \times 1.02 \sin 75^\circ)^2 \int_{\frac{2\pi}{3}}^{\frac{4\pi}{3}} \cos^2 \frac{\varphi}{2} d\varphi}{\int_{\frac{2\pi}{3}}^{\frac{4\pi}{3}} d\varphi}$$

$$\underline{\mu = .58 \text{ D}}$$

Fig 11.

Cumene hydroperoxide Dipole moment
for structure III.

$$\mu^2 = a^2 + (.62 - b + r)^2 + r^2$$

min μ comes when

$z^2 + (.62 + r - b^2)$ is min. (1)

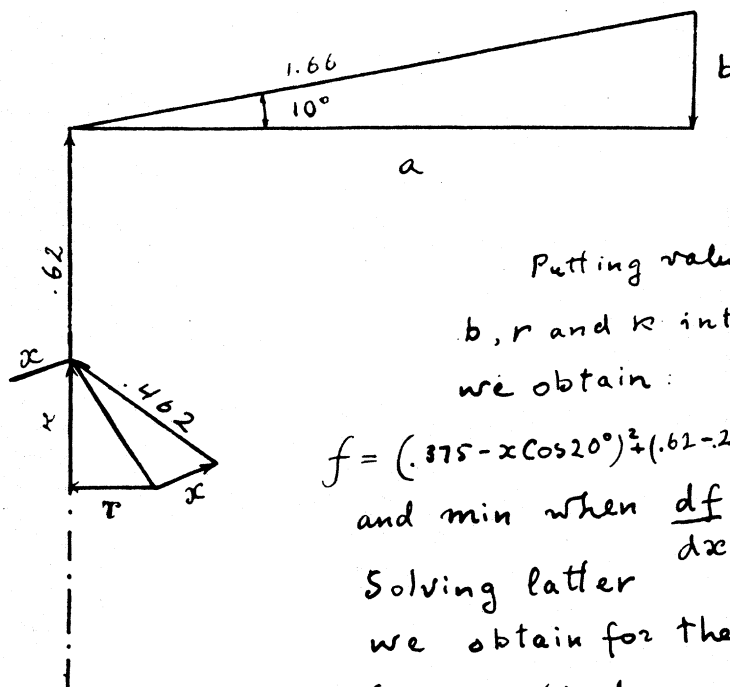
this is when $x = .15$

(Compare with Fig. 10.)

$$b = 1.66 \sin 10^\circ \approx .288$$

$$r \approx .375 - x \cos 20^\circ$$

$$r \approx .268 + x \sin 20^\circ$$



Putting values of
 b, r and r into (1)

we obtain:

$$f = (.375 - x \cos 20^\circ)^2 + (.62 - .288 + .268 + x \sin 20^\circ)^2$$

and min when $\frac{df}{dx} = 0$

Solving latter

we obtain for the x .15D

Same method was used
for calculating x with
skew structure.

$$\mu = 1.77 D$$

Fig. 12.

Perlauric acid. Model with hydrogen bonding (Giguère and Olmos), and μ for it.

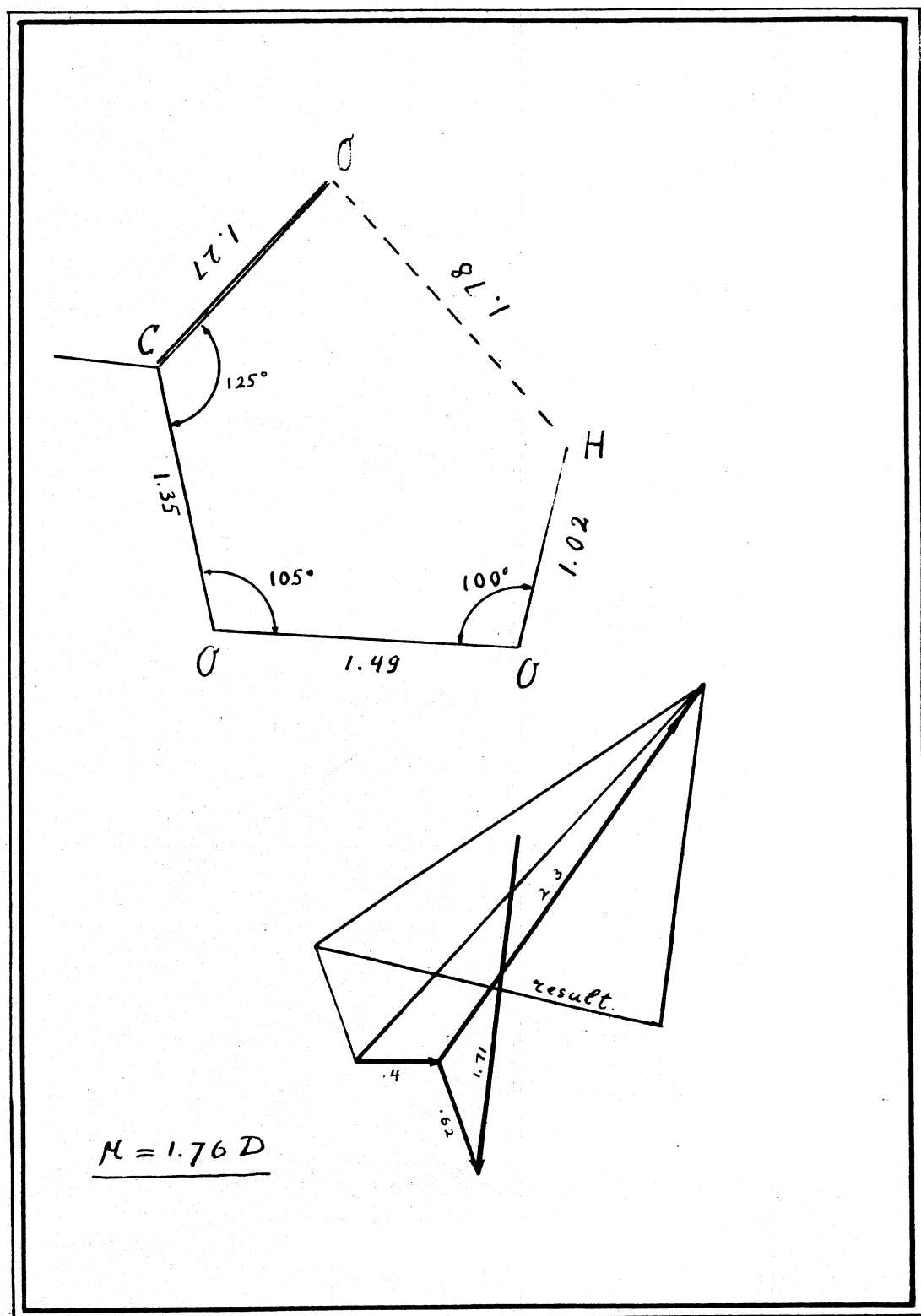


Fig. 13.

Perlauric acid. Dipole moment
for model III.

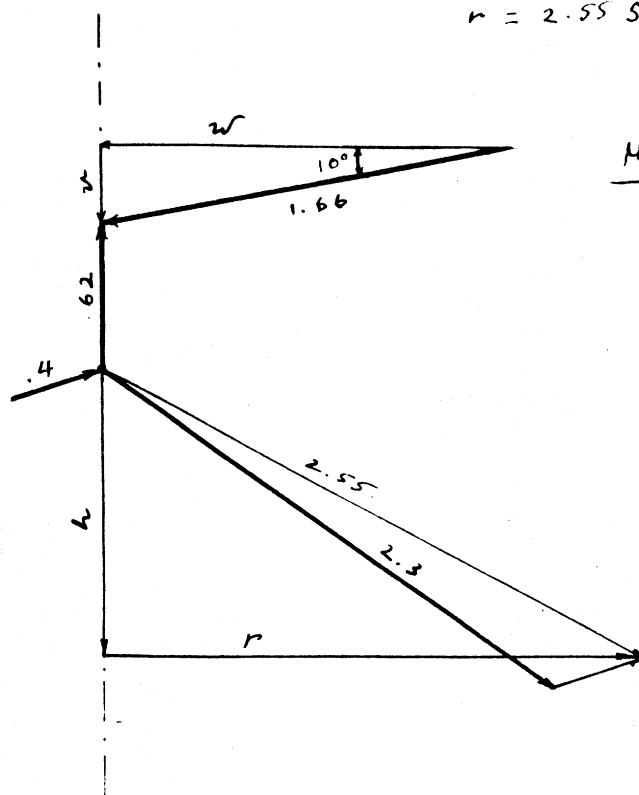
$$\bar{M}^2 = (h + v - .62)^2 + w^2 + r^2$$

$$v = 1.66 \sin 10^\circ \approx 0.30$$

$$w = 1.66 \cos 10^\circ \approx 1.63$$

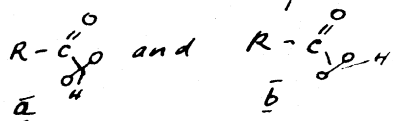
$$h = 2.55 \cos 62^\circ = 1.196$$

$$r = 2.55 \sin 62^\circ = 2.25$$



$$\mu = 2.91 \text{ D.}$$

Moments for two limiting structures



$$a) \quad \mu = \sqrt{(h + v - .62)^2 + (t + w)^2} = 3.97 \text{ D}$$

$$b) \quad \mu = \sqrt{(h + v - .62)^2 + (t - w)^2} = 1.07 \text{ D}$$

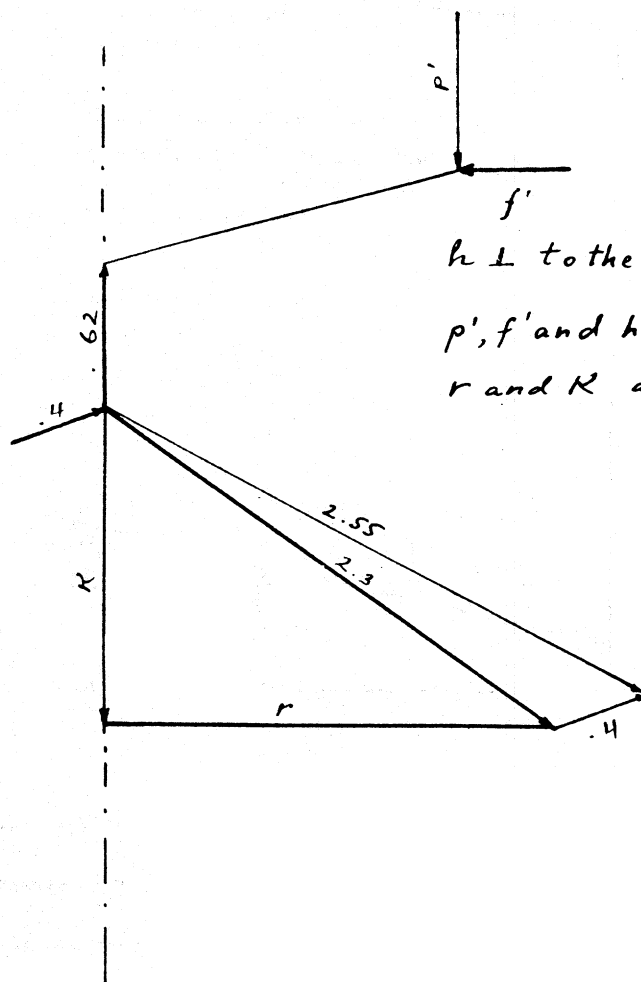
Fig. 14.

Perlauric acid. Moment for
structure I.

$$\bar{K}^2 = (h^2 + f'^2) + r^2 + (K + p' - .62)^2$$

Compare with Figs. 10 and 14.

$$\mu = 2.96 D.$$



$h \perp$ to the plane of paper.
 p', f' and h as in Fig. 10.
 r and K as in Fig. 14.

Fig. 15.

Illustration of importance of measurement of ϵ for pure solvent when working with substances having very small moment.

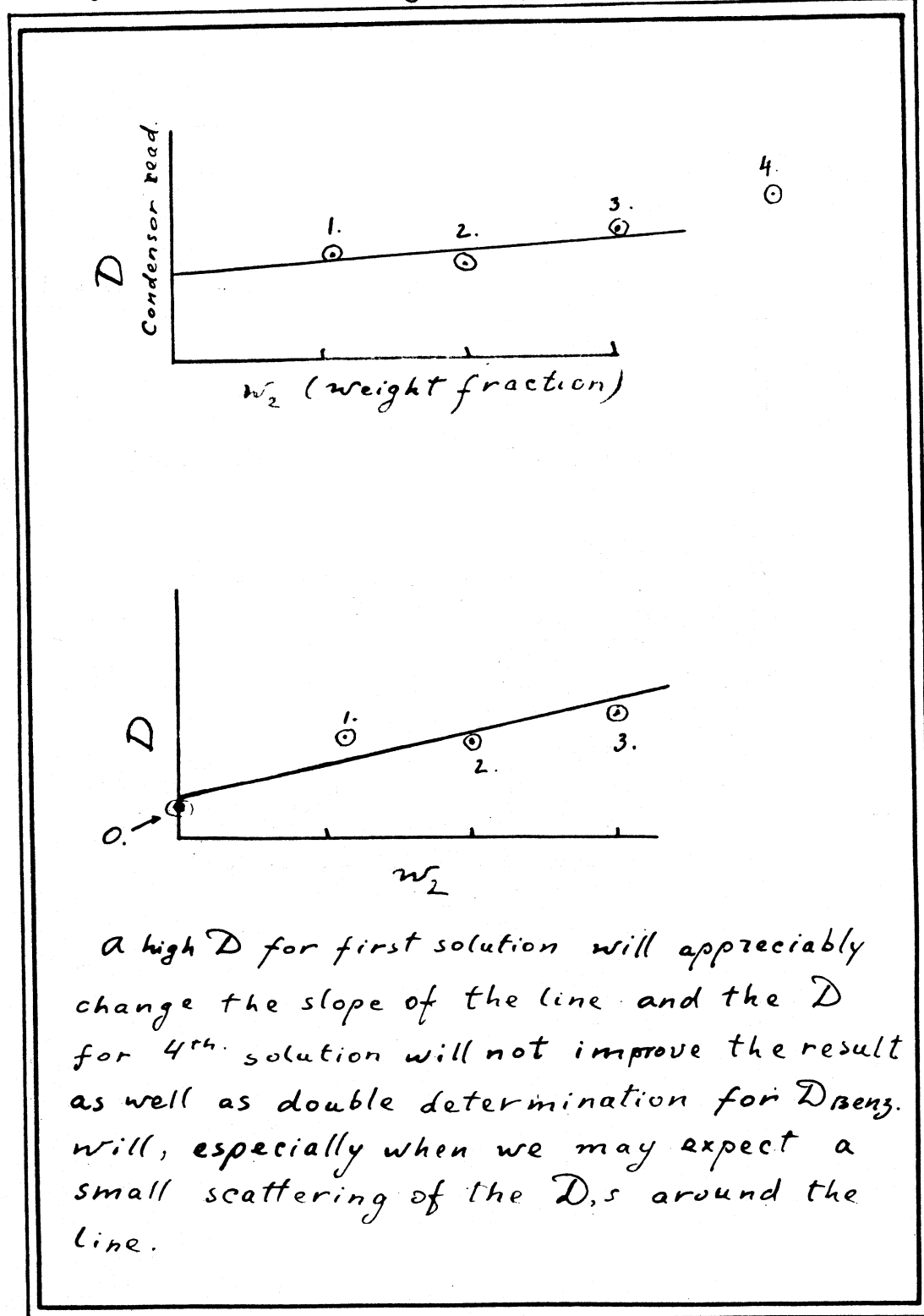


Fig. 16.